

2814 Chains, Rings and Spectroscopy

January 2003

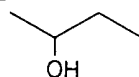
Mark Scheme

Marking structures in organic chemistry

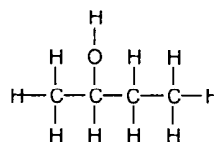
When a structure is asked for, there must be sufficient detail using conventional carbon skeleton and functional group formulae (e.g. CH_3 , C_2H_5 , OH , COOH , COOCH_3) to unambiguously define the arrangement of the atoms. (E.g. C_3H_7 would not be sufficient)

If not specified by the question, this may be given as either:

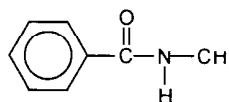
- a **structural formula** – e.g. $\text{CH}_3\text{CH}(\text{OH})\text{C}_2\text{H}_5$,



- a **skeletal formula** – e.g.



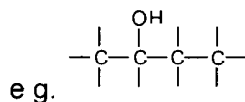
- a **displayed formula** – e.g.



or as a hybrid of these – e.g.

The following errors should be penalised – although each one only loses a maximum of one mark on the paper:

- clearly connecting a functional group by the wrong atom
- showing only 'sticks' instead of hydrogen atoms –



Benzene rings may be represented as



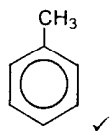
as well as



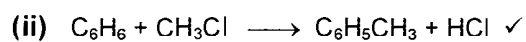
in any

¹ Note that in organic chemistry a candidate may identify a compound by name and formula. If one of these is wrong then the mark is not awarded as this is a contradictory answer.

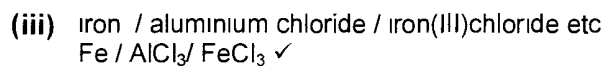
1 (a) (i)



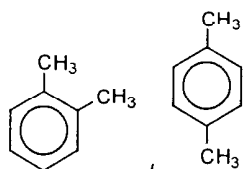
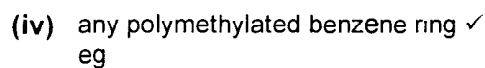
[1]



[1]



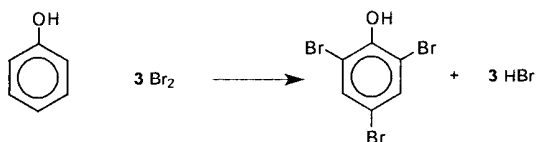
[1]



name ✓ eg 1,2-dimethylbenzene/
1,4-dimethylbenzene

[2]

(b) (i)



brominated phenol ✓ 2,4,6 substituted ✓
balancing ✓

[3]

(ii)



phenoxide ✓
balancing ✓

[2]

(c)

any general use that contains phenols - eg
antiseptics / disinfectants / dyes / plastics / pharmaceuticals / pesticides/explosives ✓

[1]

[Total: 11]

- 2 (a) (i) (trigonal) pyramidal ✓ [1]
- (ii) tetrahedral ✓ [1]
- (iii) trigonal (planar) ✓ [1]
- (b) (i) $\text{H}_3\text{N}^+\text{CH}_2\text{COOH}$ ✓ [1]
- (ii) $\text{NH}_2\text{CH}_2\text{COO}^-$ ✓ [1]
- (c) (i) H^+ / acid / HCl / H_2SO_4 / OH^- / alkali ✓
/heat / reflux ✓
(or use of an enzyme at 37°ish) [2]
- (ii) hydrolysis ✓ [1]
- (d) (i) carbon with four different / distinguishable groups attached ✓
(or carbon / part of the molecule / atom which is assymmetric / non-superimposable on its mirror image) [1]
- (ii)
- $$\begin{array}{c} \text{NH}_2 \\ | \\ \text{CH}_3 - \text{C} - \text{H} \\ | \\ \text{COOH} \end{array}$$

$$\begin{array}{c} \text{NH}_2 \\ | \\ \text{H} - \text{C} - \text{CH}_3 \\ | \\ \text{HOOC} \end{array}$$
- one structure of alanine with at least one 3-d bond ✓
two optical isomers / reflections of a 3-d structure ✓ [2]
- (iii) one stereoisomer ✓
natural / from a living system / made by enzymes etc ✓ [2]

[Total: 13]

3 (a) ester ✓
(primary) amine ✓ [2]

(b) (i) $C_8H_9NO_2$ ✓ [1]

(ii) M_r of A = 151 (or ecf from (i)) ✓

moles A = $0.100g/151 = 0.000662$

conc A = $0.000662/0.330dm^3$

= 0.002 / 0.0020 (ecf from a wrong M_r) ✓

[2]

(c) (i) peaks identified

peak X – benzene ring protons ✓

peak Y – CH_2 protons ✓

peak Z – CH_3 protons ✓

3 identification marks

reasoning from δ value . . for each, either.

- quotes the relevant functional group in the Data Sheet (eg $-O-CH_2-R$) /or
- quotes the relevant Data Sheet range (eg 3.3–4.3) / or
- from first principles using the expected deshielding to assign the peaks
✓✓✓

reasoning from the splitting pattern .

Y peak is a quadruplet/1 3 3.1 etc

this is due to 3 neighbours / adjacent to a CH_3 ✓

Z peak is a triplet / 1 2:1 etc

this is due to 2 neighbours /adjacent to a CH_2 ✓

ANY 3 out of 5 reasoning marks [6]

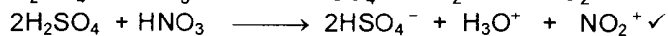
(ii) peak at $1700cm^{-1}$ and/or at $1280cm^{-1}$ marked ✓

[1]

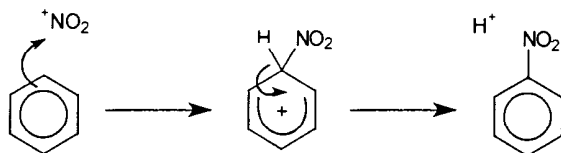
[Total: 12]

4 (a) (i) reagents conc $\text{H}_2\text{SO}_4 + \text{HNO}_3$ ✓

electrophile NO_2^+ ✓



mechanism

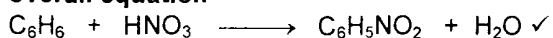


curly arrow from benzene π -bond to electrophile ✓

correct intermediate (ecf on electrophile formula) ✓

curly arrow from C-H bond to π -bond and H^+ formed ✓

overall equation



ANY 6 out of 7 [6]

(ii) NO_2^+ accepts an electron pair ✓
H is replaced / substituted by NO_2 ✓

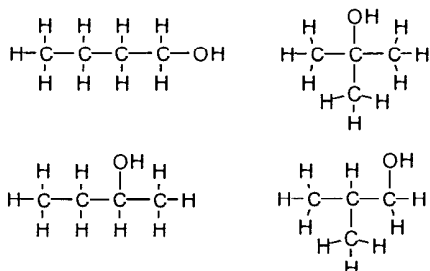
[2]

(b) two peaks ✓
peak at/between 2 3-2 7 ✓
peak at/between 7 1-7 7 ✓

[3]

[Total: 11]

5 (a)



any unambiguous type of formula ✓✓✓✓

[4]

- (b) (i) butan-1-ol gives butanal / butanoic acid / an aldehyde / a carboxylic acid
 butan-2-ol gives butanone / a ketone
 2-methylpropan-2-ol gives no reaction ✓✓✓

3 marks for the alcohol reactions

D is methylpropan-1-ol ✓

E is methylpropanoic acid ✓✓

(where any carboxylic acid for E gets the first mark)

3 marks for identifying D and E

Quality of Written Communication

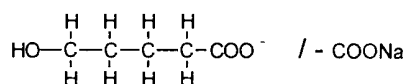
information is organised clearly and coherently using at least **two** specialist terms not mentioned in the question (eg correct names of compounds, primary, secondary, aldehyde, ketone, oxidised etc) ✓

[6]

- (ii) $(\text{CH}_3)_2\text{CHCOOH} + \text{C}_2\text{H}_5\text{OH} \longrightarrow (\text{CH}_3)_2\text{CHCOOC}_2\text{H}_5 + \text{H}_2\text{O}$
 / $\text{C}_4\text{H}_8\text{O}_2 + \text{C}_2\text{H}_6\text{O} \longrightarrow \text{C}_6\text{H}_{12}\text{O}_2 + \text{H}_2\text{O}$
 / ecf from (i) ✓

[1]

(c)



where

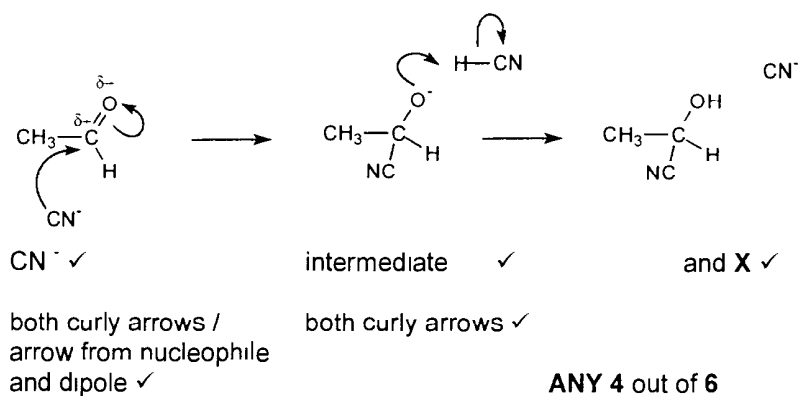
-OH ✓

-COO⁻ / COO⁻ Na⁺ / COONa ✓

2]

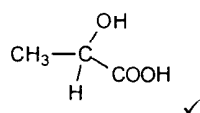
[Total: 13]

6 (a) (i) nucleophilic addition ✓

(ii) $\text{HCl} / \text{H}_2\text{SO}_4 / \text{H}^+ / \text{acid}$ ✓
hydrolysis ✓

[2]

(iii)



[1]

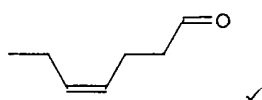
(b) 1 doublet and 1 quadruplet / 1 3 3 1 and 1.1 ✓
correct reason for at least one peak ✓
(eg 1,3 3,1 due to 3 neighbours / next to CH_3 / use of $n+1$ rule)

[2]

(c) (i) $\text{C}_7\text{H}_{12}\text{O}$ ✓

[1]

(ii)



[1]

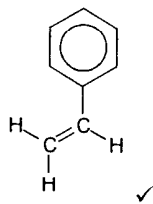
(iii)



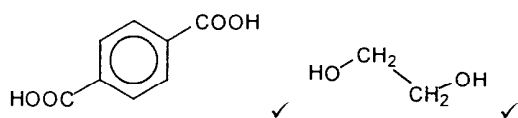
[2]

[Total: 13]

7 (a) L:

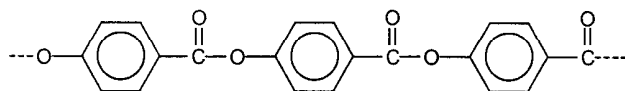


M:



[3]

(b)



at least one correct ester link ✓

rest of the structure and repeat also correct ✓

[2]

(c)

condensation ✓

loss of water / small molecule ✓

[2]

(d)

fibres / clothing / bottles etc ✓

[1]

[Total: 8]

8 to detect the presence of C=O ...

2,4-dinitrophenylhydrazine / 2,4-DNPH ✓
red/orange/yellow ppt/solid/crystals ✓

or

i r spectrum ✓
has peak at 1680-1750 cm⁻¹ ✓

2 marks

to confirm it is a ketone not an aldehyde ...

Tollens' reagent / (acidified) K₂Cr₂O₇ ✓
aldehyde: silver mirror / green colour ✓
ketone: no silver mirror / no green colour ✓

or

n m r. spectrum ✓
aldehyde: peak at 9.5-10 ✓
ketone: no peak at 9.5-10 ✓

3 marks

a chemical method to identify the ketone ...

use the product / solid / ppt from 2,4-DNPH / 2,4-dinitrophenylhydrazine ✓
(re)crystallise / purify (the product) ✓
measure the melting point ✓
compare with known compounds / data book ✓

4 marks

ANY 8 marks out of 9 [8]

Quality of Written Communication

at least two sentences with legible text, accurate spelling, grammar and punctuation, so the meaning is clear ✓

[1]

[Total: 9]